Multicolor IR spectroscopy of pure liquid water

Cringus, Dan; Pshenichnikov, Maxim S.; Wiersma, Douwe A.; Mostovoy, Maxim; Lindner, Jörg; Vöhringer, Peter

Published in:
Ultrafast Phenomena XV, Proceedings of the 15th International Conference

Multicolor IR Spectroscopy of Pure Liquid Water

Dan Cringus[1], Maxim S. Pshenichnikov[1], Douwe A. Wiersma[1], Maxim Mostovoy[2], Jörg Lindner[3], and Peter Vöhringer[3]

[1] Department of Physical Chemistry, [2] Institute for Theoretical Physics
Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
E-mail: M.S.Pchenitchnikov@RuG.nl
[3] Lehrstuhl für Molekulare Physikalische Chemie, Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-Wilhelms-Universität, Wegelerstraße 12, 53115 Bonn, Germany
E-mail: jlindner@uni-bonn.de

Abstract. Multicolor infrared ultrafast spectroscopy is applied to investigate the vibrational relaxation dynamics in liquid water at room temperature with both the stretching and the bending mode being photoexcited and probed. A unified model, capable of the reproduction of as much as 150 transients, yielded cross-sections and relaxation times for the stretching and bending modes. It is demonstrated, that the energy from the initially excited stretching vibration is partitioned to the bending modes of approximately two water molecules.

Recent advances in femtosecond infrared (fs-IR) spectroscopy have brought about considerable progress in unraveling various molecular dynamical phenomena in water [1,2], in particular vibrational energy relaxation (VER). In neat liquid water VER is quite complex because of numerous intra- and intermolecular resonances (Fig. 1a): the stretching mode is resonant with the first bending overtone of the same molecule (Fermi resonance) and to two bending quanta partitioned over pairs of molecules. Furthermore, stretching and bending vibrations of different molecules are coupled via a hydrogen bond network, and their coupling to librations and hindered translations leads to extensive vibrational line broadenings. The efficient mixing of all intra- and intermolecular modes suggests that VER could be governed by collective phenomena [3].

Despite all remarkable efforts during the last years, consensus has been reached neither on the detailed relaxation channels nor on identifying intermediate state(s) involved in the stretching relaxation. More importantly, it still remains unresolved, whether the relaxation occurs within the initially excited molecule alone or collectively by dissipating and/or delocalizing the energy to neighboring water molecules.

In this contribution, we present extensive time- and frequency resolved fs-IR data in both the bending and the stretching mode spectral region to unravel the vibrational relaxation pathways. It is demonstrated that the stretch decay produces almost exactly two bends. A proposed unified relaxation model is fully capable of describing the experimental results.

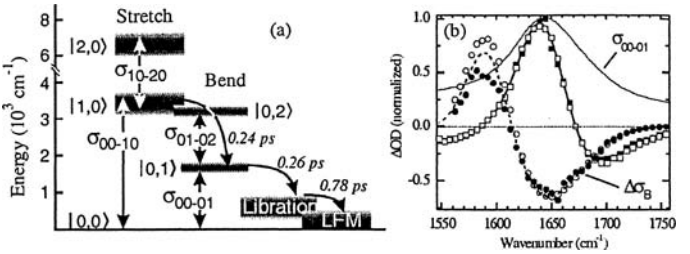

Fig.1. (a): Energy level diagram of the kinetic model for vibrational relaxation in liquid water with the following abbreviations for cross sections: $\Delta\sigma_S = \sigma_{10-20} - 2\sigma_{00-10}$, $\Delta\sigma_B = \sigma_{01-02} - 2\sigma_{00-01}$, and $\Delta\sigma_C = \sigma_{01-11} - \sigma_{00-10}$. LFM stands for low-frequency modes. (b): Bend and thermal (i.e., at 8 ps delay) cross-sections (circles and squares, respectively) following bending (open symbols) and stretching (closed symbols) excitation. The thin solid line shows the bend absorption.

Pump-probe experiments of the four possible combinations of exciting and detecting the bending and the stretching mode have been performed. Two independently tunable optical parametric amplifiers (~0.2 ps cross-correlation time) and a monochromator with a dual-row MCT array for wavelength-selective detection were used. Pump energies were about 6 μJ for the stretch excitation (at 3300 cm^{-1}) and 2.5 μJ for the bend excitation (at 1650 cm^{-1}). The polarizations between pump and probe pulses were set to magic angle. The 2 μm thick liquid water sample was contained in a rotating cell with CaF_2 windows.

A total of 150 pump-probe transients following excitation of the bending or the stretching vibration were recorded. In all cases, the signals approach a steady state level with a time constant of ~0.8 ps indicating a common final relaxation step that is associated with the final thermalization process. The transients presented in Fig. 2 are particularly sensitive to short-time relaxation processes which are otherwise hidden underneath the thermalization of heating. The *stretch-stretch* transient first decays and then recovers with time constants of 0.24 ps and 0.26 ps, respectively. While the rapid decay can be assigned to the depopulation of the initially-excited stretching mode [4-7], the subsequent recovery requires further clarification. The *stretch-bend* transient peaks with a noticeable retardation of

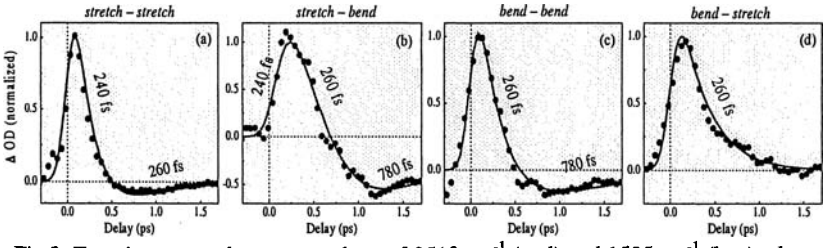

Fig.2. Transients at probe wavenumbers of 3510 cm^{-1} (a, d) and 1585 cm^{-1} (b, c) where the thermal background at long delays is almost zero. The *stretch-stretch* transient is inverted for ease of comparison. Solid curves resulted from the global fit procedure using a complete data set of 150 time-resolved transients.

~0.25 ps and then decays with the time constant of ~0.26 ps already seen in the *stretch-stretch* experiment. Since the similar time constant is also present in the *bend-bend* experiment, the first excited state of the bending vibration must have a lifetime of 0.26 ps [8] and must relax through an intermediate state before heating the probe volume. For energetic reasons, this intermediate state belongs to the librational manifold and exhibits a lifetime of 0.8 ps. This assignment is further supported by a pronounced kinetic isotope effect observed in complementary measurements on heavy water, where this time constant is increased by a factor of $\sqrt{2}$ to 1.1 ps. Finally, the direct bend excitation leads to an instantaneous change of the stretching absorption cross-section that decays with the bending lifetime constant of 0.26 ps (Fig. 2d).

The proposed relaxation model for vibrationally excited H_2O is shown in Fig. 1a. A global fit yielded relaxation times for the first excited states of the stretching vibration (0.24 ps), the bend vibration (0.26 ps) and the librations (0.78 ps) as well as the corresponding cross-sections. To allow a direct comparison of transient cross-sections obtained in different experiments, the transient spectra at delays of ~8 ps (when the relaxation is finished resulting in a heated water sample) were matched to each other. Identical temperature jumps require twice as much water molecules to be excited for the bending than for the stretching mode. Therefore, the near equality of the cross-sections $\Delta\sigma_B$ from *bend-bend* and *stretch-bend* experiments implies that *relaxation of the stretch quantum produces almost two bend quanta.* Note that the applied normalization naturally accounts for intrinsic experimental variations as excitation fluxes, focusing conditions, optical densities etc. An identical value of splitting ratio of ~2 was also obtained from *bend-stretch* and *stretch-stretch* experiments.

The following relaxation sequence emerges from the analysis: The initial stretch excitation migrates over several adjacent water molecules after which the bend overtone is excited due to its nonlinear intramolecular coupling with the (symmetric) stretching mode. The bend overtone acts as a transition state with its energy being immediately (faster than 50 fs) split between two bends of neighboring molecules. The bend excitations are further transferred in parallel to adjacent water molecules or librations. Finally, the librational excitation is transferred to the low-frequency modes hereby completing the relaxation process. The preliminary results of numerical simulations show that a cluster of ~30 water molecules is required to accommodate the initial stretch excitation.

References

1 R. Rey, K.B. Møller, and J.T. Hynes, Chem. Rev. **104**, 1915 (2004).
2 E.T.J. Nibbering and T. Elsaesser, Chem. Rev. **104**, 1887 (2004).
3 S. Woutersen and H. J. Bakker, Nature **402,** 507 (1999).
4 A.J. Lock and H.J. Bakker, J. Chem. Phys. **117**, 1708 (2002).
5 D. Cringus *et al.*, Chem. Phys. Lett. **408**, 162 (2005).
6 M.L. Cowan *et al*, Nature **434**, 199 (2005).
7 J. Lindner *at al.*, Chem. Phys. Lett. **421**, 329 (2006).
8 N. Huse *at al.*, Chem. Phys. Lett. **404,** 389 (2005).